



Short communication

Carbon dioxide gas sensor using a graphene sheet

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ABSTRACT

In this article, we report on a high-performance graphene carbon dioxide (CO₂) gas sensor fabricated by mechanical cleavage. Unlike other solid-state gas sensors, the graphene sensor can be operated under ambient conditions and at room temperature. Changes in the device conductance are measured for various concentrations of CO₂ gas adsorbed on the surface of graphene. The conductance of the graphene gas sensor increases linearly when the concentration of CO₂ gas is increased from 10 to 100 ppm. The advantages of this sensor are high sensitivity, fast response time, short recovery time, and low power consumption.

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1. Introduction

The increased emission of carbon dioxide (CO₂) and other greenhouse gases since the mid-20th century has been thought to be the cause of the increase in the average near-surface air and ocean temperature of the earth, a phenomenon known as global warming. Efforts are being undertaken to mitigate the greenhouse gas concentration by monitoring and subsequently reducing CO₂ emission from the combustion of fuel in vehicles and the burning of coal in power plants. Therefore, it is important to develop low-cost, sensitive, resettable sensors that can be used to monitor the CO₂ concentration in industrial exhaust gases.

Since the development of the first solid-state gas sensor by Seiyama [1], several other research groups have been attempting to make improvements to gas sensors, with the aim of enhancing the sensing performance. For the past several years, carbon nanotubes (CNTs) have been considered promising candidates for sensing materials that can detect extremely low concentrations (ppb range) of gases such as NO₂, NH₃, O₂, H₂, CO₂, and CO [2–8]. The high sensitivity of CNT-based gas sensors can be attributed to the excellent electrical properties, small size, high surface-to-volume ratio, and large gas-adsorption capacity of CNTs. More recently, graphene, a two-dimensional monolayer of carbon atoms, has been identified

to be a promising sensing material because it has unique and excellent electrical and mechanical properties [9–12]. Graphene has very high electron mobility at room temperature, and hence, its sensitivity is very high. Graphene devices are expected to have relatively low Johnson noise and 1/*f* noise because of their high conductance and low crystal defect density, respectively [10]. Graphene is more suitable for device integration than are CNTs because the planar nanostructure of the former makes it advantageous for use in standard microfabrication techniques. In addition, the recent improvements made to graphene deposition methods have contributed to an increase in the applicability of graphene for device integration [13,14]. In this study, we demonstrate the features of a CO₂ gas sensor fabricated from a graphene sheet by mechanical cleavage. We also evaluate the sensing characteristics of the gas sensor during its operation under atmospheric conditions.

2. Experimental details

The graphene samples used in this study were prepared by a previously reported stamping method [15–18]. First, polydimethylsiloxane (PDMS, Sylgard 184, Dow-Corning) stamps were fabricated by mixing PDMS and a curing agent in 10:1 ratio and pouring the mixture into a stamp mold for curing. After curing at 80 °C, the sticky PDMS stamps that were freshly peeled off from the mold were used to transfer thin highly ordered pyrolytic graphite (HOPG, SPI-1 grade) flakes (or graphene) to the surfaces of thermally oxidized Si substrates (300 nm oxide thickness) on which Au alignments were prefabricated. With this method,

Abbreviations: PDMS, polydimethylsiloxane; HOPG, highly ordered pyrolytic graphite; PMMA, polymethylmethacrylate; MFC, mass flow controller.

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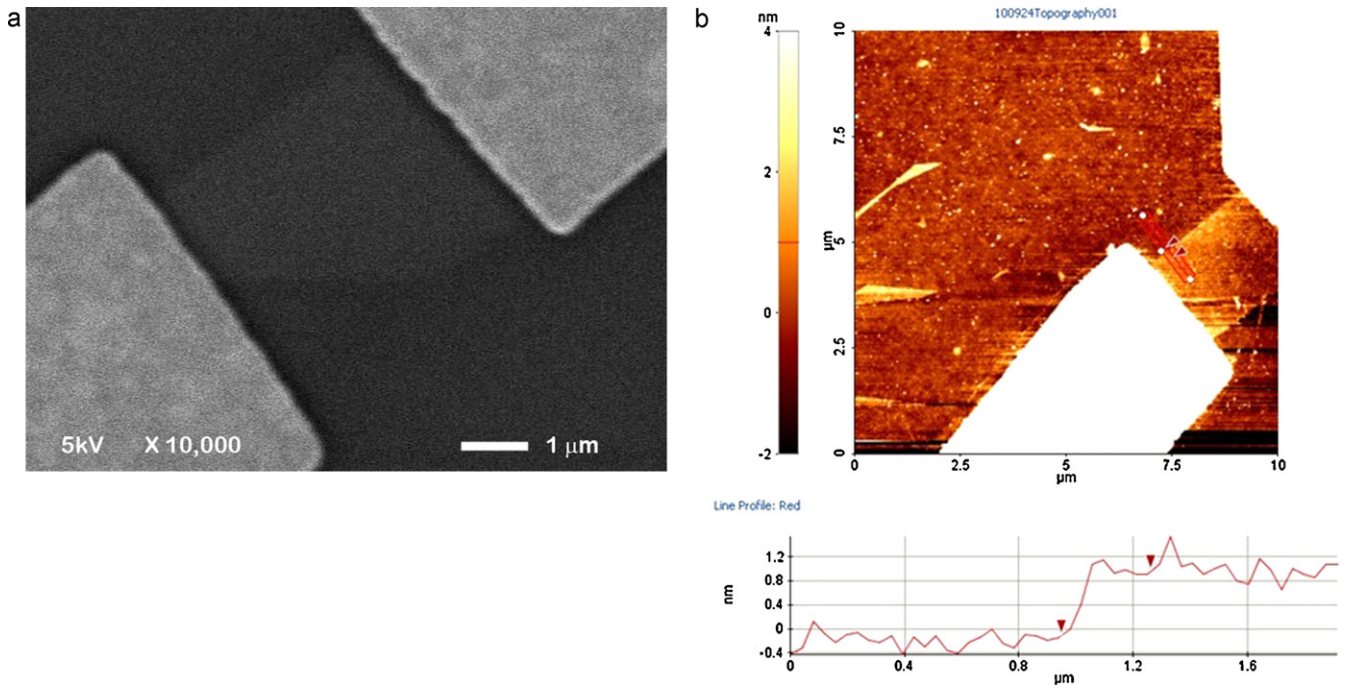


Fig. 1. (a) SEM image and (b) AFM image of graphene and electrodes.

graphene flakes could be deposited at specific locations on the substrate, and further, the amount of residue left behind on the substrate was considerably lesser than that when using the traditional mechanical cleavage method, in which “Scotch tape” is

employed. Graphene flakes were identified using an optical microscope and located with respect to the Au alignment marks [19]. The thickness of graphene flakes was measured by atomic force microscopy (AFM). The substrate was coated with two layers of

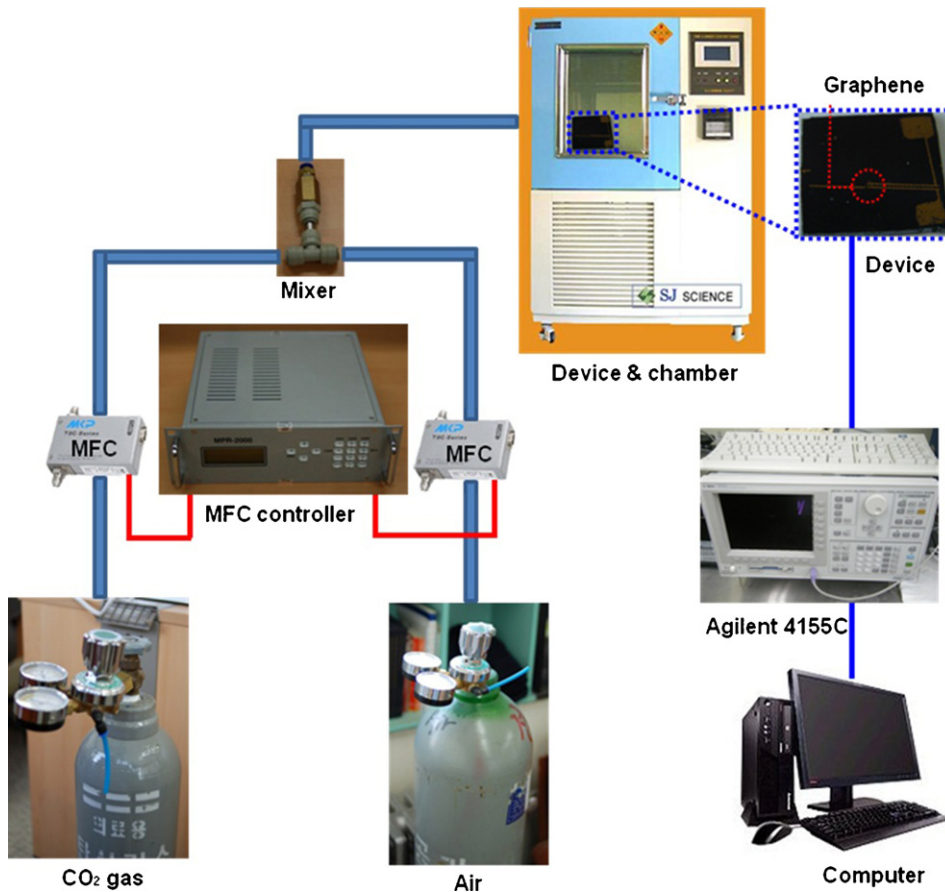


Fig. 2. Experimental setup for measurements performed using the graphene CO₂ gas sensor.

polymethylmethacrylate (PMMA), which was used as an electron beam resist material to afford easy liftoff (first layer: PMMA 495A, 8% in anisole; second layer: PMMA 950A, 4% in anisole). The windows for electrical contacts to the selected graphene samples were patterned using standard electron-beam lithography. Then, a 5-nm-thick chromium adhesion layer and a 50-nm-thick gold layer were deposited by electron-beam evaporation. Finally, liftoff was completed in a Remover PG (Microchem) solution at 70 °C. Fig. 1(a) shows the scanning electron microscopy (SEM) image and Fig. 1(b) shows the AFM image of graphene connected with two electrodes. The thickness of the graphene layer was about 1.2 nm, as determined by AFM. The dimensions of the graphene layer were about $3 \mu\text{m} \times 3 \mu\text{m}$, and it was mostly uniform.

To characterize the performance of the fabricated graphene device as a CO₂ sensor, we measured its electrical transport properties upon exposure to CO₂ gas at different concentrations. As illustrated in Fig. 2, the graphene CO₂ gas sensor was placed inside a constant-temperature, constant-humidity chamber connected to a two-input mixer that mixes the CO₂ gas and the compressed air; the temperature and humidity of the chamber were precisely controlled. The compressed air used was a mixture of highly purified nitrogen (79%) and oxygen (21%). The flow rates of CO₂ and air were controlled by mass flow controllers (MFCs). The concentration of CO₂ gas was varied from 10 to 100 ppm by adjusting the flow rates of CO₂ and air. A semiconductor parameter analyzer (Agilent 4155 C) was used to measure the conductance of the graphene devices.

3. Results and discussion

Fig. 3(a) shows the I – V characteristics of the graphene gas sensor depicted in Fig. 1. The applied voltage ranged from -0.5 V in 10-mV steps. The current increased as the applied voltage was increased. For gas-sensing applications, a V_d value of 0.3 V was used, and the resistance was estimated to be 1.4 k Ω at room temperature (22 °C, 44% humidity).

Fig. 3(b) shows the time response of the graphene CO₂ gas sensor in the presence of CO₂ at different temperatures. The chamber is initially filled with air. At 30 s, 100 ppm of CO₂ gas is infused into the chamber. After the infusion of CO₂ gas, the conductance increases abruptly at the beginning, then gradually levels off until it reaches a steady-state value. The y -axis $(G_g - G_a)/G_a$ represents the ratio of the change in the electrical conductivity in ambient air, where G_a and G_g are the conductance of the graphene before and after the addition of CO₂ in ambient air, respectively. The CO₂ gas molecule adsorption on a graphene sheet can induce an increase in graphene conductance. The CO₂ gas molecule acts as a donor/acceptor on the graphene sheet. The graphene conductance change indicates a charge transfer between CO₂ gas and the graphene sheet. Hence, the physical adsorption of CO₂ gas on the graphene sheet is the dominant sensing mechanism [10,20–22]. The large increase in conductance ($\sim 26\%$) shows that CO₂ can be adsorbed on the graphene sheet very effectively. The response time of CO₂ gas detection is 8 s. The response time is defined as the time taken for the relative conductance change to reach 90% of the steady-state value. The average recovery time is about 10 s. The short recovery time can be attributed to the weak interaction between the CO₂ gas molecules and graphene. The interaction of graphene with CO₂ is very different from the interaction of graphene with other gas molecules (such as NH₃ and NO₂), and hence, several hours of high-temperature annealing in vacuum is not required to remove the adsorbed CO₂ gas molecules [10]. This implies that on graphene, CO₂ molecules are more easily adsorbed or desorbed than are other gas molecules. The response time of the device remains unchanged even when experiments are repeated at

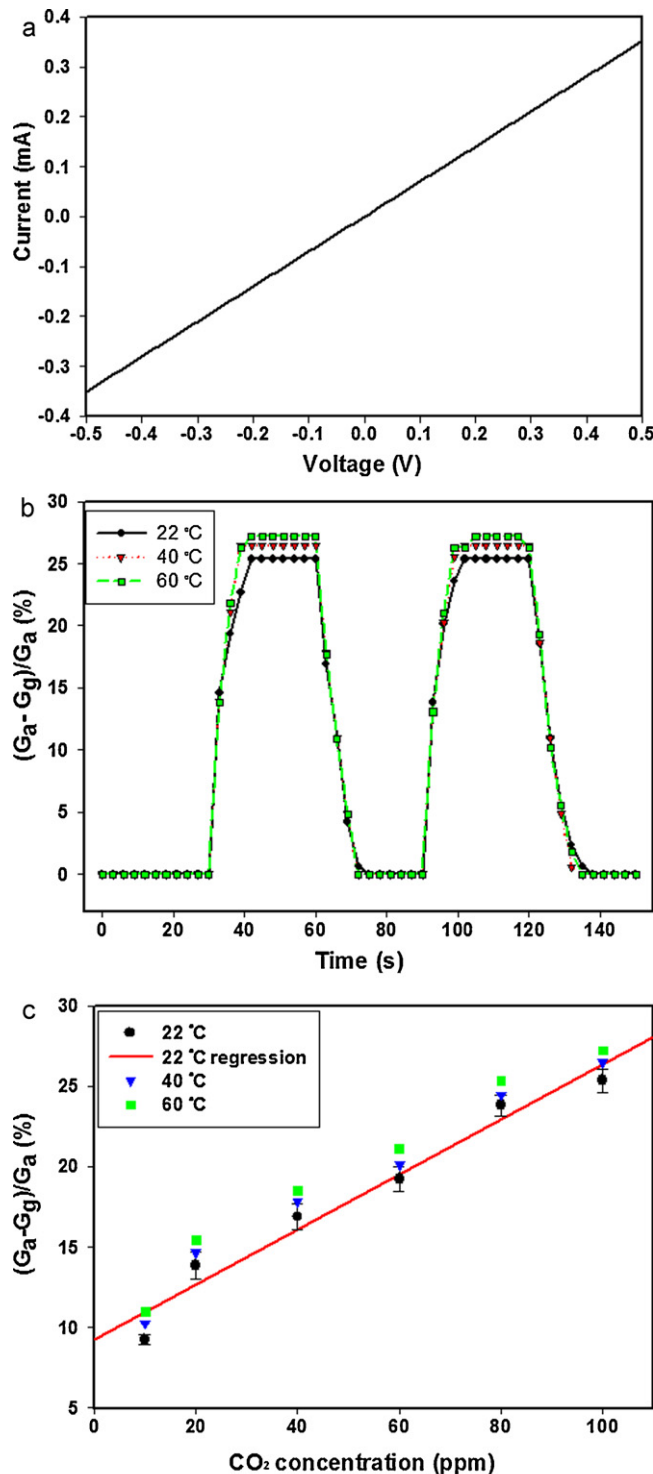


Fig. 3. (a) I – V curve obtained for the fabricated graphene gas sensor; (b) time response of the graphene CO₂ gas sensor in the presence of 100 ppm CO₂, at different temperatures; (c) conductance changes at different concentrations of CO₂.

different temperatures (22, 40, and 60 °C). The conductance change observed when the graphene gas sensor is exposed to CO₂ gas at 40 °C and 60 °C (4.37% and 7.27%, respectively) is different from that observed at 22 °C.

The ratio of conductance change to various concentrations of CO₂ is shown in Fig. 3(c). As the concentration of CO₂ increased from 10 to 100 ppm at 22 °C, 44% humidity, the ratio of conductance change increased from 9% to 26%. The estimated CO₂ sensitiv-

ity of the sensor for the measurement range was 0.17%/ppm. We repeated the experiments three times at the same concentration, and the error was less than 0.8%. The experimental results demonstrated that the sensor response was highly reproducible.

4. Conclusions

In this article, we report on a graphene-based CO₂ gas sensor fabricated by mechanical cleavage and micromachining. Graphene can be transferred to a silicon substrate by PDMS stamping. The graphene sensor shows significant conductance changes when exposed to various concentrations of CO₂ in air. The response time of the sensor is less than 10 s, suggesting that the device shows fast response to CO₂ gas. Because of the weak interaction between CO₂ and graphene, the device response is rapid and reproducible. In the future, we will investigate the feasibility of using graphene sensors for environmental monitoring and carry out surface functionalization of the graphene layers to enhance the selectivity of the sensor.

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